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Raman Spectroscopy Study of Solvation Structure in Acetonitrile/Water Mixtures

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by

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TTL03

SEN03 1 **Raman Spectroscopic Study of Solvation Structure in**  
ADR03 2 **Acetonitrile/Water Mixtures**

AUT03 3 Kathy L. Rowlen<sup>1</sup> and Joel M. Harris\*

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ABS03

SEN03 1 Raman spectroscopy is used to probe the CN stretching fre-  
11 quency of acetonitrile as a function of concentration in water.  
SEN06 1 The CN band is modeled as the sum of two Gaussians. The  
SEN09 3 concentration dependence of area and width for each of the  
SEN12 20 Gaussian components provides experimental support of an  
3 equilibrium between two forms of acetonitrile in solution. In  
12 addition the concentration dependence of each of the bands  
SEN15 18 correlates well with the thermodynamically related Kirk-  
6 wood-Buff Integrals ( $G_H$ ). Specifically, both the vibrational  
16 band width and  $G_H$  exhibit maxima near  $X_{CH_3CN} \approx 0.3$ , sug-  
SEN18 1 gestive of strong interaction between acetonitrile molecules.  
12 The frequency shift of the CN band exhibits a linear depen-  
12 dence on the dielectric constant of protic solvents.

TXT03

SEN03

PAR03

INTRODUCTION

SEN03 1 There has been considerable effort to define and understand  
11 the fundamental molecular interactions important in liquid  
SEN06 18 chromatography (1-3). Although the solvophobic theory (1)  
7 is commonly invoked to explain retention in reversed-phase  
15 liquid chromatography (RPLC), recent studies have pointed  
SEN09 22 out shortcomings in this model (3, 4). Using statistical  
thermodynamics, Dill (4) has demonstrated that retention in  
12 RPLC is driven by two classes of interactions: (1) the dif-  
23 ferences in chemical interactions of the solute in each of the  
14 phases, which affect the enthalpy of the system, and (2)  
SEN12 44 changes in the entropy of the system. Studies of the im-  
5 portance of chemical interactions with the solvent have em-  
13 ployed such techniques as solute solvatochromism (5, 6).  
SEN15 1 Solvent-stationary phase interactions have also received at-  
SEN18 8 tention (7, 8). It is clear that the solvent plays a crucial role  
12 in establishing the "structure" of the stationary phase, which,  
SEN21 21 in turn, impacts the nature of solute retention. Recently  
1 several studies of solvent-stationary phase behavior have  
19 employed environment-sensitive probe molecules, such as  
SEN24 16 pyrene, adsorbed or immobilized at the surface (9). Spec-  
2 troscopic changes in the probe provide information about the  
11 solute but only an indirect measure of surface characteristics.  
SEN27 3 An important experiment for understanding solute-induced  
4 changes in either the solvent-phase structure or the station-  
16 ary-phase structure would involve monitoring some charac-  
22 teristic of the solvent and/or stationary phase directly. The  
SEN30 21 motivation for understanding solvent structure is found in the  
12 work recently conducted by Wirth (10, 11), in which the im-  
22 portance of shape selectivity in retention (related to structural  
11 order) was demonstrated spectroscopically.

PAR06

SEN03 1 Acetonitrile ( $CH_3CN$ ) is one of the most widely used organic  
12 modifiers in reversed-phase liquid chromatography; it also has  
29 significant application in nonaqueous electrochemistry (12).  
SEN06 1 The Raman spectrum of  $CH_3CN$  has unique features in re-  
13 gions of low spectral interference; therefore, Raman spec-  
14 troscopy of  $CH_3CN$  is an excellent choice for a direct probe  
29 of solvent microenvironment.

PAR09

SEN03 1 The CN stretch in acetonitrile exhibits a rather unique shift  
12 to higher frequency when hydrogen bonded (13) or coordi-  
SEN06 20 nated with Lewis acids (14). On the basis of the analogous  
4 situation encountered with carbonyls, in which the CO stretch  
7 shifts to lower frequency when hydrogen bonded (15), one  
26 expects that coordination of the nitrogen lone pair electrons  
SEN09 35 would lengthen and thus weaken the CN bond. In the case  
5 of carbonyls,  $^{13}C$  nuclear magnetic resonance (NMR) studies  
11 show an apparent reduction in electron density (a shift to  
13 lower fields) about the carbonyl carbon and presumably an  
32 accompanying increase in electron density about oxygen, as  
40 the concentration of a hydrogen bond donor is increased (16).  
SEN12 1 Similarly, NMR studies of  $CH_3CN$ -water mixtures show that

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**TXT03**  
**PAR09**

the  $^{14}\text{N}$  resonance shifts to higher fields, an apparent increase in electron density about the nitrogen (17). Sadlej and Keck (18) employed a modified CNDO method to study the electronic structure of acetonitrile and its complexes with metal cations. They attributed the increased force constant of the CN bond to a rehybridization in which the  $2p\sigma$  character of the lone pair is increased. Consideration of the partial antibonding character of nitrogen's  $2p\sigma$  orbital led to the conclusion that the removal of the lone pair electrons enhances the CN bond order. The authors observed that the corresponding restructuring of  $\pi$  electrons would account for the increased electron density about N (as measured by NMR). An increase in the force constant of the CN bond readily accounts for the observed shift to higher frequencies when  $\text{CH}_3\text{CN}$  is hydrogen bonded (13, 19).

**PAR12**

The liquid structure of  $\text{CH}_3\text{CN}$  is also of interest and remains unresolved. Strong molecular interactions must account for the high boiling point of  $\text{CH}_3\text{CN}$  (82 °C) as well as the fact that  $\nu_{\text{CN}}$  is 13  $\text{cm}^{-1}$  higher in the gas phase than in liquid (20). For comparison, the boiling point of methanol (similar density and molecular weight), which exists as a hydrogen-bonded network in solution, is only 64.7 °C. It has been proposed that a liquid-phase antiparallel alignment of two  $\text{CH}_3\text{CN}$  molecules would result in a reduced dipole moment, therefore a weaker CN bond (21). This concept is supported by the observation that a single  $\text{CH}_3\text{CN}$  molecule in the gas phase has a dipole moment of 3.92 D, whereas the gaseous dimer has a dipole moment of 2.67 D (14). There is a large body of work that suggests that  $\text{CH}_3\text{CN}$  is partitioned between monomers and dimers in solution (14, 20, 22). Griffiths (23) indicated that it is unreasonable to expect a true  $\text{CH}_3\text{CN}$  dimer to exist in solution and that free or unassociated  $\text{CH}_3\text{CN}$  is likely to be in equilibrium with some undefined self-associated form of  $\text{CH}_3\text{CN}$ . Temperature-dependent studies of  $\text{CH}_3\text{CN}$  in a variety of solvents appear to indicate that monomeric or free  $\text{CH}_3\text{CN}$  does not exist in solution; rather,  $\text{CH}_3\text{CN}$  is organized as aggregates or loosely defined clusters (24). Several researchers have reported that the CN stretching band of  $\text{CH}_3\text{CN}$  in the liquid phase is composed of two overlapped Gaussians: a narrow band, attributed to the monomeric or free form of  $\text{CH}_3\text{CN}$ , and a broad band, attributed to some organized form of  $\text{CH}_3\text{CN}$  (13, 23, 24). Infrared matrix isolation studies of  $\text{CH}_3\text{CN}$  show two resolved bands in the CN stretching region (14).

**PAR15**

In order to employ  $\text{CH}_3\text{CN}$  and Raman spectroscopy as a direct probe of solute/solvent or solvent/stationary phase interactions, it is first necessary to understand the nature of vibrational perturbations arising from solvent/solvent interactions. Here we report a detailed Raman spectroscopic study of  $\text{CH}_3\text{CN}$  in water. Presented in this work is the behavior of the CN stretching vibration over the entire concentration range of acetonitrile/water mixtures and an exploration of the relationships between observed frequency shifts and solvent properties. Two groups have recently investigated the vibrational spectroscopy of  $\text{CH}_3\text{CN}$ /water mixtures (13, 19), focusing primarily on the structural composition of water; neither group modeled the vibrational band structure. This work mathematically models the CN stretching band ( $\nu_{\text{CN}}$ ) as the sum of two Gaussians, whose behavior as a function of concentration supports the concept of an equilibrium between at least two distinct  $\text{CH}_3\text{CN}$  species in solution. Further support for such an equilibrium is found in the strong correlation between the CN frequency shift and the dielectric constant of a variety of hydrogen-bond donor solvents.

**TXT06**

**PAR18**

All solvents were spectrochemical or UV grade and were stored over molecular sieves ( $4\text{ \AA} \times 1/16$  in.). Doubly distilled, HPLC grade (Omnisolve) water was used in all experiments involving water.

**PAR21**

The 514.5-nm line from an argon ion laser (Lexel Model 95) was employed as the excitation source. Plasma lines from the source were eliminated with a combination of two Pellin Brocha

**EXPERIMENTAL SECTION**

**TXT06**  
**PAR21**

prisms (Optics for Research, ABDO-20) and a variable aperture. The 30-mW beam was focused to approximately 80  $\mu\text{m}$  at the sample cell, a 0.1- $\times$  1-cm glass capillary (Kimax). Sample introduction was achieved via a 5-mL syringe connected to the capillary with 0.8-mm-i.d. Teflon tubing. All measurements were conducted at ambient temperature. Light from the cell was collected and collimated at 90° from excitation by a  $f/2$  camera lens (Canon, f1 50 mm) and then focused at the entrance slit of the spectrograph (0.5 m, Spex 1870) with a  $f/3.9$  planoconvex lens. The entrance slit width was 60 (or 80)  $\mu\text{m}$  in all cases, corresponding to a spectral bandwidth of 3.6  $\text{cm}^{-1}$ . A colloidal glass (RG-530, Schott) high-pass filter, placed in front of the entrance slit, served to remove scattered source light. A 600 grove/mm grating dispersed the light across a Thomson THF7882CDA charge-coupled device (CCD, Photometrics). With the long axis (576 channels) oriented in the direction of wavelength dispersion, a spectral region of approximately 600  $\text{cm}^{-1}$  was sampled simultaneously at approximately 1  $\text{cm}^{-1}$ /channel. The CCD controller was linked to a Mac IIcx via a general purpose interface board (GPIB, National Instruments). The interface software, OMA, was written by Marshall Long (Yale, Applied Physics Department).

**PAR24**

For all spectra presented in this work, a preflash was used and the charge from 384 columns was binned along the slit axis for signal-to-noise improvement. It has recently been reported that binning in this direction can result in artificial band broadening (25). However, we are confident that the asymmetry found in the bands reported herein is physicochemical in nature based on the fact that similar band shapes have been observed and reported by workers using monochromator-PMT systems (13, 23, 24) and the following study of charge trapping conducted in this lab. The effect of charge trapping on peak parameters was quantified by using a single Lorentzian fit to the 214- $\text{cm}^{-1}$  band of  $\text{CCl}_4$ . We found charge trapping to be of concern only at low signal intensities, <70,000 photoelectrons, in which no "preflash" had been used to uniformly irradiate the CCD. With the preflash, no band distortions were observed.

**PAR27**

The CH, CN, and CC stretching frequencies (2942, 2249, 918  $\text{cm}^{-1}$  (26)) in dry  $\text{CH}_3\text{CN}$  were used as reference points for band position measurements in other solvents. These reference points were established prior to each set of measurements in a given region. To avoid mechanical backlash errors, the spectrograph settings were not varied during any group of measurements in a particular region. All quantitative measurements were made, minimally, in triplicate. Concentrations (M) were calculated taking into account the nonideal volume of mixing for  $\text{CH}_3\text{CN}$  and water, as tabulated by Katz et al. (27). Measured band areas were corrected for refractive index effects as indicated by Bauer et al. (28). The correction values vary less than 2% over the investigated concentration range.

**PAR30**

Data processing was conducted on an IBM AT compatible computer. Conversion of binary files from the Macintosh disk operating system to MS-DOS was carried out with the Apple File Exchange program. Peak modeling to Gaussian functions was achieved with the program Curvefit ( $\chi^2$  minimization) in SpectraCalc (Galactic Industries, V2.1). The spectra could not be modeled as Lorentzian functions.

**TXT09**

**RESULTS AND DISCUSSION**

**PAR33**

**Acetonitrile in Water. CN Stretch.** Figure 1 shows the CN stretching band ( $\nu_{\text{CN}}$ ) in neat acetonitrile. The frequency maximum shifts linearly to higher frequencies as the molar concentration of  $\text{CH}_3\text{CN}$  in water decreases, from 2249  $\text{cm}^{-1}$  in neat  $\text{CH}_3\text{CN}$  to 2256  $\text{cm}^{-1}$  at 1.9 M (a change of  $7 \pm 0.4$   $\text{cm}^{-1}$ , from eight measurements). In order to investigate the possibility and behavior of overlapped bands as a function of concentration, both  $\nu_{\text{CN}}$  and  $\nu_1$ , as labeled in Figure 1, were modeled by using the Curvefit program in Spectra Calc.  $\nu_1$  is a combination band arising from the symmetric bend of CH, and the CC stretch (29). Although  $\nu_1$  is not part of the CN stretch, it was included in the model in order to improve the accuracy of the fit. The best fit to the CN band shape is two overlapped Gaussians ( $\nu_{\text{H}}$  and  $\nu_{\text{HH}}$ ).

**PAR36**

**Band Area.** As is observed from Figure 2, the total measured area ( $\nu_{\text{H}} + \nu_{\text{HH}}$ ) is linear with concentration. Figure 3 shows the behavior of  $\nu_{\text{H}}$  and  $\nu_{\text{HH}}$  as a function of concentration. Assuming that both  $\nu_{\text{H}}$  and  $\nu_{\text{HH}}$  are due only to the stretching mode of CN (30), the fact that there are two bands, each

FIG 1 (009, 3- 4)

FIG 2 (006, 7- 8)  
FIG 3 (009, 3- 4)

**TXT09**  
**PAR36**

26 having a unique concentration dependence, implies that  
33 acetonitrile exists in at least two distinct forms in solution.  
SEN15 1 Since both  $\nu_{\text{H}}$  and  $\nu_{\text{H}}$  are present in pure (dry)  $\text{CH}_3\text{CN}$ , neither  
24 of the two Gaussian components can be attributed to hydrogen  
SEN18 24 bonding with water. This may not be true for low concen-  
SEN21 9 trations of  $\text{CH}_3\text{CN}$  in water. Both components have nearly  
6 equivalent areas from 2 to 8 M  $\text{CH}_3\text{CN}$  which, in agreement  
17 with previous observations (20, 24), suggests that strong in-  
25 teractions between  $\text{CH}_3\text{CN}$  molecules must prevail even at  
SEN24 33 low concentrations. Between 8 and 12 M, the area of  $\nu_{\text{H}}$   
SEN27 11 increases at a rate faster than that of  $\nu_{\text{H}}$ . Near 12 M ( $X_{\text{CH}_3\text{CN}}$   
6  $\approx 0.3-0.35$ )  $\text{CH}_3\text{CN}$ , there appears to be a transition between  
SEN30 16  $\nu_{\text{H}}$  and  $\nu_{\text{H}}$ . At concentrations greater than 15 M ( $X_{\text{CH}_3\text{CN}} \approx$   
SEN33 10  $0.55$ ),  $\nu_{\text{H}}$  becomes the dominant band. The relationship be-  
4 tween areas at concentrations greater than 12 M is consistent  
14 with a picture of the liquid in which self-associated  $\text{CH}_3\text{CN}$ ,  
24 represented by  $\nu_{\text{H}}$ , is favored at high concentrations.

**PAR39**

SEN03 1 Attempts to quantify a particular species, such as  $\text{CH}_3\text{CN}$   
11 monomer or dimer, using the measured band areas were un-  
SEN06 20 successful. Substitution of activity (31) for molality did not  
SEN09 10 improve the situation. However, as Pimentel and McClellan  
7 (32) have pointed out, one would only expect a clear, definable  
18 equilibrium between, for example, monomer and dimer in  
26 solution if the dimer were cyclic with no additional sites  
SEN12 36 available for interaction. Consideration of the data presented  
7 here and evidence that the methyl group is strongly involved  
17 in determining the structure of liquid  $\text{CH}_3\text{CN}$  (33) lead to the  
28 conclusion that no simple equilibrium between definite  
35  $\text{CH}_3\text{CN}$  species exists in solution.

**PAR42**

SEN03 1 **Bandwidth.** Figure 4 shows the bandwidth (full width at  
SEN06 10 half maximum) as a function of mole fraction  $\text{CH}_3\text{CN}$ ; mole  
29 fraction is used in this case, rather than molality, to facilitate  
SEN09 31 comparison with thermodynamic parameters. Note, however,  
4 that the maximum in bandwidth occurs at the same concen-  
23 tration as the transition observed for band areas ( $\approx 12$  M).

**PAR45**

SEN03 1 Matteoli and Luciano (34) recently calculated the values  
10 of  $G_{ij}$  for  $\text{CH}_3\text{CN}$ -water mixtures from the Kirkwood-Buff  
18 integrals (35)

$$G_{ij} = (g_{ij} - 1)4\pi r^2 dr \quad (1)$$

20 where  $g_{ij}$  is the radial distribution function and  $r$  is the average  
SEN06 32 distance between adjacent molecules.  $G_{ij}$  is a measure of the  
8 tendency for dissimilar molecules to interact and  $G_{ii}$  is a  
SEN09 18 measure of interaction tendency between like molecules.  $G_{ij}$   
1 and  $G_{ii}$  are related to thermodynamic properties as described  
12 by the following equations

$$G_{ij} = RTK_T - V_i/V_j DV \quad (2)$$

$$G_{ii} = G_{ij} + V_j/(D - V_i)x_i \quad (3)$$

$$D = 1 + x_i(\partial \ln \alpha_i / \partial x_i)_{T,P} \quad (4)$$

26 where  $R$ ,  $T$ ,  $K_T$ ,  $V_i$ ,  $\alpha_i$ ,  $x_i$ , and  $V$  represent the gas constant,  
29 temperature, isothermal compressibility coefficient of the  
35 solution, partial molar volume, activity coefficient, mole  
42 fraction, and the volume per mole of mixture, respectively.  
SEN12 1 Matteoli and Luciano found, for both  $\text{CH}_3\text{CN}$  and water, that  
SEN15 12  $G_{ij}$  exhibited a maximum near  $X_{\text{CH}_3\text{CN}} = 0.3 (=X_{\text{max}})$ . Such  
1 a maximum implies a strong tendency for like molecules to  
11 associate ( $G_{ii}$  vs  $X_i$  decreases monotonically for an ideal  
SEN18 22 mixture). On the basis of the overall shape of the  $G_{ij}$  vs  $X_i$   
14 curve, the authors divided the solution behavior into three  
23 categories, the maximum serving as the transition between  
SEN21 31 solvation and self-association. At  $X_{\text{CH}_3\text{CN}} < X_{\text{max}}$ , the trend  
9 of  $G_{ij}$  for water indicated that small amounts of  $\text{CH}_3\text{CN}$  could  
SEN24 19 significantly affect the structure of water. The structure of  
5  $\text{CH}_3\text{CN}$  remains primarily unaffected by small amounts of  
SEN27 13 water. At  $X_{\text{CH}_3\text{CN}} > X_{\text{max}}$ , the authors noted that the smooth  
2 trend of  $G_{ij}$  toward neat  $\text{CH}_3\text{CN}$  was suggestive of direct  
22 interaction between  $\text{CH}_3\text{CN}$  molecules.

**PAR48**

SEN03 1 The bandwidths of both  $\nu_{\text{H}}$  and  $\nu_{\text{H}}$  exhibit a maximum near  
SEN06 13  $X_{\text{CH}_3\text{CN}} = 0.3$ . The maximum is more pronounced for  $\nu_{\text{H}}$   
9 (self-associated  $\text{CH}_3\text{CN}$ ); thus, the behavior of the bandwidth

FIG 4 (006, 3-4)



REQU 1 (003,19-20)

REQU 2 (009,15-16)

REQU 3 (009,15-16)

REQU 4 (009,15-16)

TXT09  
PAR48

may be more closely associated with  $\text{CH}_3\text{CN}$ - $\text{CH}_3\text{CN}$  interactions rather than  $\text{CH}_3\text{CN}$ - $\text{H}_2\text{O}$  interactions. Since both the bandwidths and band areas undergo dramatic transitions at the concentrations of similar activity for the Kirkwood integrals, there appears to be a relationship between the solvent structure probed by Raman spectroscopy and the thermodynamic properties of the solution. In addition, it is interesting to note that the bandwidth maximum occurs at precisely the point at which the partial molar excess volumes of  $\text{CH}_3\text{CN}$  and water are equal (36). Kamagawa and Kitagawa (33), using Raman difference spectroscopy to analyze the symmetric CH stretch of  $\text{CH}_3\text{CN}$  in water, found that a plot of homogeneous frequency shift (the shift attributed to self-associated molecules) vs mole fraction was very similar to the plot of partial molar volume vs mole fraction. The authors interpreted this as an indication that the frequency shift was related to the structure of the solution.

PAR51

*Frequency Shifts.* Figure 5 shows the center frequency of  $\nu_{\text{CH}}$  and  $\nu_{\text{CN}}$  vs mole fraction. The measured center frequency for  $\nu_{\text{CN}}$  is dominated by  $\nu_{\text{CH}}$  and therefore exhibits similar behavior. For the purpose of discussion, we will assume that an  $\text{CH}_3\text{CN}$  dimer is representative of self-associated  $\text{CH}_3\text{CN}$ . Thomas and Thomas-Orville proposed the structure of an  $\text{CH}_3\text{CN}$  dimer as

RGID AC5B11a (015.12-13)

This structure also derives from both neutron diffraction studies and ab initio calculations as the most energetically stable  $\text{CH}_3\text{CN}$  dimer orientation for intermolecular distances less than 5 Å (22). According to Pauling (37), due to the large dipole moment, the CN bond can possess as much as 21% ionic character. Bulk solvent effects, such as dielectric properties, are therefore expected to play a key role in determining the strength of intermolecular interactions. If self-association results in a lower CN force constant, through partial cancellation of dipole moments—as mentioned in the Introduction—then the effective solvation of self-associated  $\text{CH}_3\text{CN}$  should result in an increase in  $\nu_{\text{CN}}$ . Hydrogen bonding, in which the partially antibonding lone pair electrons are removed from the CN bond, should also result in an increase in  $\nu_{\text{CN}}$ . Therefore, in the case of protic solvents, the magnitude of shift in  $\nu_{\text{CN}}$  is expected to have a complicated dependence on both solvent dielectric properties and hydrogen-bond strength. It is worth noting that the center frequency of  $\nu_{\text{CH}}$  exhibits a linear dependence on molarity, whereas  $\nu_{\text{CH}}$  has a more complicated dependence. The dielectric constant of  $\text{CH}_3\text{CN}$ -water mixtures varies approximately linearly with molarity (38). In addition to dielectric and hydrogen-bond effects, there is evidence that suggests that hydrophobic interactions may also play a role in  $\text{CH}_3\text{CN}$  aggregation at high water concentrations (33, 34).

PAR54

To test the importance of dielectric effects, a study of  $\text{CH}_3\text{CN}$  ( $X_{\text{CH}_3\text{CN}} = 0.037$ , 1.9 M) in a variety of protic (hydrogen-bond donating) solvents was conducted. Figure 6 shows the frequency shift from 2249  $\text{cm}^{-1}$  ( $\nu_{\text{CN}}$  in pure  $\text{CH}_3\text{CN}$ ) as a function of dielectric constant. The frequency shift for  $\text{CH}_3\text{CN}$  would, of course, be zero but is not shown on the graph because it is not a hydrogen-bond donor. Note that water ( $\epsilon = 78.5$ ) is the only solvent in the figure that has a higher dielectric constant than  $\text{CH}_3\text{CN}$  ( $\epsilon = 38.8$ ). The difference in the magnitude of shift for water and its nearest neighbor (MeOH) is significant. The linearity of the plot as well as the magnitude of the shift for water indicates a strong dependence on the dielectric properties of the solvent. Plots of frequency shift vs (1) dipole moment, (2) refractive index, (3) polarizability (calculated from the Clausius-Mossotti equation), and (4) orientation polarizability ( $\Delta f$ ) (calculated from the Linnert equation (39)) were all nonlinear or uncorrelated. For the above calculations, it was assumed that the bulk properties of the mixture were equivalent to those of the solvent. This assumption is valid for dilute solutions, as is true for  $X_{\text{CH}_3\text{CN}} = 0.037$ . Although bulk dielectric properties appear to play a primary role in determining  $\nu_{\text{CN}}$ , hydrogen bonding must also take place. Recent ab initio calculations have estimated

FIG 5 (006, 3-4)



FIG 6 (006, 3-4)



TXT09  
PAR54

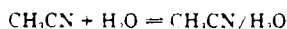
the hydrogen-bond strength of  $\text{CH}_3\text{CN}$ -water to be approximately 4 kcal/mol (41). The OH stretch of water is quite sensitive to dilution with  $\text{CH}_3\text{CN}$ , shifting more than  $100\text{ cm}^{-1}$  over the concentration range studied. The magnitude of the shift is characteristic of hydrogen-bond donors (42).

## PAR57

Both the CC and CH stretching modes shift to higher frequency upon dilution of  $\text{CH}_3\text{CN}$  in water. The slopes of center frequency vs molarity are 0.39 and 0.27 for  $\nu_{\text{CC}}$  and  $\nu_{\text{CH}}$ , respectively.

## PAR60

*Associated Species.* Katz et al. (27) recently suggested that mixtures of MeOH, water,  $\text{CH}_3\text{CN}$ , water, and tetrahydrofuran (THF)-water should be regarded as ternary solvent systems, the three components being free solvent, i.e., not associated with water, free water, and a solvent/water complex. The authors postulated that deviation from ideal mixing, as well as chromatographic anomalies, could be explained in terms of the presence of this third (solvent/water) species. They mathematically modeled the volume of the mixing curve by assuming that the molar volume of all three components remained constant over the entire range of compositions. However, it is well documented that the molar volume of components in nonideal solutions does indeed vary (42). In addition, in describing  $\text{CH}_3\text{CN}$ -water mixtures as a simple equilibrium



$$K_{\text{eq}} = [\text{CH}_3\text{CN}/\text{H}_2\text{O}]/[\text{CH}_3\text{CN}][\text{H}_2\text{O}] \quad (5)$$

the activities of water,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  must be used to calculate  $K_{\text{eq}}$ . Based on the activities reported by French (31), the equilibrium in eq 5 would result in an  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  complex whose activity remains constant from 0.2 to 0.7 mole fraction  $\text{CH}_3\text{CN}$ . The model used by Katz et al. results in a continuously varying associated complex (as measured by volume fraction) that exhibits a maximum near  $X_{\text{CH}_3\text{CN}} = 0.25$ . Based on the results of Matteoli and Luciano (34), the minimum in the volume of mixing may be due to effective "packing" of  $\text{CH}_3\text{CN}$  within the water structure rather than a maximum in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  complexes. While it is intuitively satisfying to consider associated species in binary mixtures, the model Katz et al. have chosen may not be an accurate description.

## PAR63

Taking into account both solvent/solvent and solvent/solute species,  $\text{CH}_3\text{CN}$ -water mixtures are more thoroughly described as having at least six general components:  $(\text{CH}_3\text{CN})_n$ ,  $(\text{CH}_3\text{CN}/\text{H}_2\text{O})_n$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and  $(\text{H}_2\text{O})_n$ . As the concentration is varied, the distribution of interactions must also vary. At low  $\text{CH}_3\text{CN}$  concentrations ( $X_{\text{CH}_3\text{CN}} < 0.3$ ), due to the strength of attractive forces between  $\text{CH}_3\text{CN}$  molecules, it is not unreasonable that both free (e.g.,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ) and self-associated (e.g.,  $\text{CH}_3\text{CN}/\text{CH}_3\text{CN}$ )  $\text{CH}_3\text{CN}$  exist. The stable association of  $\text{CH}_3\text{CN}$  molecules would eventually serve to disrupt the water structure. Based on the observations of Singh and Krueger (19), in which the  $3225\text{-cm}^{-1}$  band in water vanishes as  $\text{CH}_3\text{CN}$  is increased to  $X_{\text{CH}_3\text{CN}} = 0.47$ , the structure of water appears to be dominant up to  $X_{\text{CH}_3\text{CN}} = 0.3$ . Beyond that point, both the structure of water and of  $\text{CH}_3\text{CN}$  approach their least structural form. The maximum excess entropy of mixing ( $X_{\text{CH}_3\text{CN}} = 0.55$ ), rather than the volume of mixing, is likely to be correlated with the largest degree of association between  $\text{CH}_3\text{CN}$  and water (see Figure 7 (31, 43)). At  $\text{CH}_3\text{CN}$  mole fractions greater than 0.55, the structure of  $\text{CH}_3\text{CN}$  dominates. This concept is supported by the fact that the area of band III, attributed to self-associated  $\text{CH}_3\text{CN}$ , becomes the dominant factor at  $\text{CH}_3\text{CN}$  mole fractions greater than 0.55.

## PAR66

Although there are undoubtedly a variety of effects that influence the degree of association between  $\text{CH}_3\text{CN}$  molecules, it is possible that the dominant driving force for aggregation progresses from hydrophobic to electrostatic as the  $\text{CH}_3\text{CN}$  concentration is increased. At high water concentrations, the dielectric constant of the solution is high; therefore, electrostatic interactions are minimized while the tendency for hy-

REQU 5a (018.11-12)

REQU 5 (018.11-12)

FIG 7 (021.34-35)

**TXT09**  
**PAR66**

SEN09 23 hydrophobic interactions is maximized. As mentioned above,  
5 the shape of the  $G_{\text{H}}$  vs.  $X_{\text{CH}_3\text{CN}}$  curve suggests that for  $X_{\text{CH}_3\text{CN}}$   
17  $> 0.3$  direct interactions between  $\text{CH}_3\text{CN}$  molecules occurs.  
SEN12 1 If one defines direct interaction as that which occurs at in-  
20 termolecular separation distances  $\leq 5$  Å, the antiparallel  
orientation of two  $\text{CH}_3\text{CN}$  molecules is the most stable dimer  
SEN15 30 (27). A dimer, in which the opposite partial charges are  
21 aligned, seems reasonable at high  $\text{CH}_3\text{CN}$  concentrations.  
SEN18 1 High  $\text{CH}_3\text{CN}$  concentrations would facilitate stronger elec-  
4 trostatic attraction via decreased average intermolecular  
14 distances and a lower dielectric constant.

**PAR69**

SEN03 1 *Chromatographic Implications.* The presence of a variety  
SEN06 7 of  $\text{CH}_3\text{CN}$  species in solution would result in complicated  
SEN09 16 equilibria for solvation of other solutes. Shifts in the equilibria,  
6 which occur as the solvent composition is varied, may account  
SEN12 16 for anomalies in chromatographic retention (44). McCormick  
and Karger (45) have reported the adsorption isotherms for  
MeOH,  $\text{CH}_3\text{CN}$ , and THF on a hydrophobic stationary phase  
SEN15 21 (C-18). Both  $\text{CH}_3\text{CN}$  and THF exhibited dramatic maxima  
near 50% ( $X_{\text{CH}_3\text{CN}} = 0.25$ ) and 70% (v/v) organic modifier,  
SEN18 13 respectively. For acetonitrile-water mixtures, more than twice  
as much  $\text{CH}_3\text{CN}$  is adsorbed to the surface at mobile-phase  
SEN21 18 composition  $X_{\text{CH}_3\text{CN}} = 0.25$  than at  $X_{\text{CH}_3\text{CN}} = 0.55$ . In ac-  
3 cordance with the solvophobic theory, the authors attributed  
11 the decreased adsorption of the organic modifier to reduced  
water concentration in the mobile phase, water being the  
SEN24 1 driving force for removal of organic modifier from solution.  
However, the removal of organic modifier from solution is  
SEN27 1 unlikely to be driven by entropy, since (1) the process of  
concentrating solvent-solute at the interface is accompanied  
SEN30 21 by a decrease in entropy due to structuring of the alkyl phase  
(3, 4) and (2) the solvation of  $\text{CH}_3\text{CN}$  in water is purely en-  
23 tropy driven (see Figure 7). If hydrophobic expulsion were  
exclusively responsible for concentrating  $\text{CH}_3\text{CN}$  at the sur-  
SEN33 1 face, the process should be most favorable when the enthalpy  
of mixing is least favorable, and such is not the case. As shown  
in Figure 7, the interaction between  $\text{CH}_3\text{CN}$  and water is most  
SEN36 21 endothermic (least favorable) at mole fractions much higher  
than the observed maximum in the isotherm.  
SEN39 1 These conclusions are in agreement with studies that suggest  
that hydrophobic expulsion is not the dominant interaction  
in RPLC retention (3).

**PAR72**

SEN03 1 As mentioned previously, Katz et al. (27) suggest that  
SEN06 7 anomalies in solute retention can be explained in terms of  
associated solvent species, each of which has unique inter-  
actions with the stationary phase. As the mobile phase is  
SEN09 24 varied, the chemical characteristics of the stationary phase  
are determined by the relative concentrations of the individual  
SEN12 11 species (e.g.,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ ). The spectroscopic  
evidence presented here, in conjunction with thermodynamic  
SEN15 16 considerations, supports this proposal. The activity of  $\text{CH}_3\text{CN}$   
in water increases drastically over the range  $X_{\text{CH}_3\text{CN}} = 0-0.25$ ,  
SEN18 28 at which point it levels off (31). Based on the area and  
bandwidth behavior of  $\nu_{\text{II}}$  and  $\nu_{\text{III}}$ , the region of increasing  
SEN21 1 activity may be due to changes in the ratio of hydrogen-bonded  
to self-associated species. The minimal changes in  $\text{CH}_3\text{CN}$   
SEN24 24 activity at high  $\text{CH}_3\text{CN}$  concentrations may be due to the  
formation of a stable self-associated  $\text{CH}_3\text{CN}$  complex. The  
maximum in the adsorption isotherm reported by McCormick  
SEN27 1 and Karger (45) corresponds to the transition point in activity  
and quite closely with the transition in  $\text{CH}_3\text{CN}$  microenvi-  
29 ronment as reported here.

**TXT12**

**CONCLUSION**

**SEN03 1**

**PAR75**

**SEN03 1**

Raman spectroscopy has been used to quantify vibrational  
SEN06 16 frequency changes in acetonitrile under hydrogen-bond con-  
ditions. The CN band of acetonitrile was shown to consist  
SEN09 11 of overlapped Gaussians (II and III). The behavior of bands  
II and III as a function of concentration in water provides  
SEN12 24 experimental support for an equilibrium between  $\text{CH}_3\text{CN}$   
species in solution. Comparison of band behavior with the  
Kirkwood-Buff  $G$  values demonstrates a relationship between  
SEN15 21 solute microenvironment and the thermodynamic properties  
of the solution. The center frequency of the individual bands



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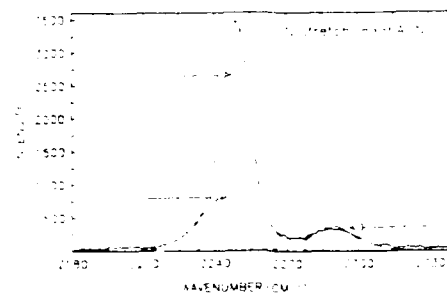


Figure 1: CN stretch (2249 cm<sup>-1</sup>) in neat acetonitrile with a 10-s integration time. The dashed lines represent the modeled Gaussians. The data are unsmoothed.

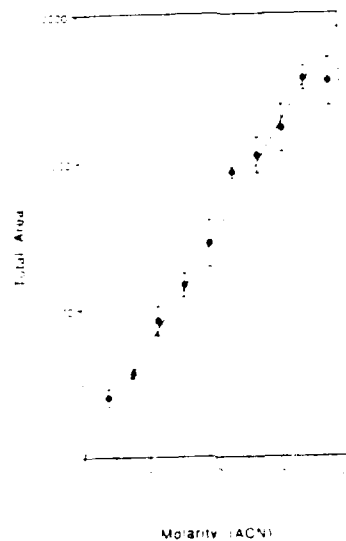


Figure 2: Total area as a function of concentration. error bars are  $\pm 2$ . The equation for the line is  $y = 1458 (\pm 34)x$ .

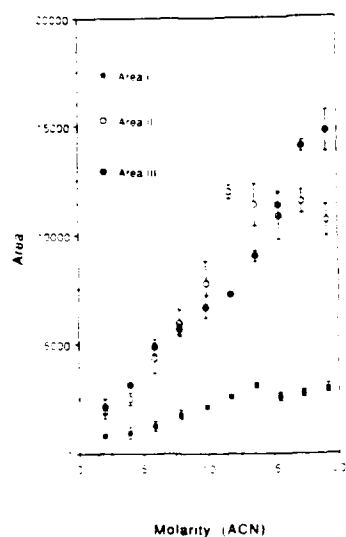


Figure 3 Area of individual Gaussian components as a function of CH<sub>3</sub>CN molarity. In some cases, the symbol width exceeds the measured error.

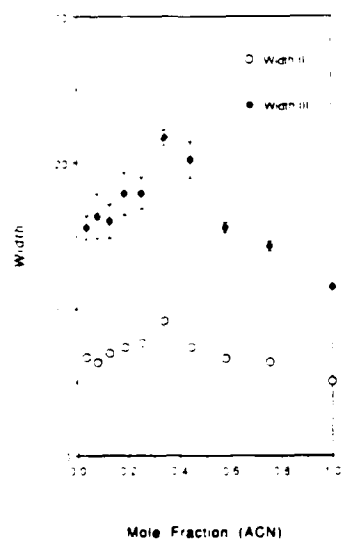


Figure 4 Bandwidth (full width at half-maximum) as a function of concentration. error bars are  $\pm \sigma$ . For band II, the symbol width is larger than the measured error.

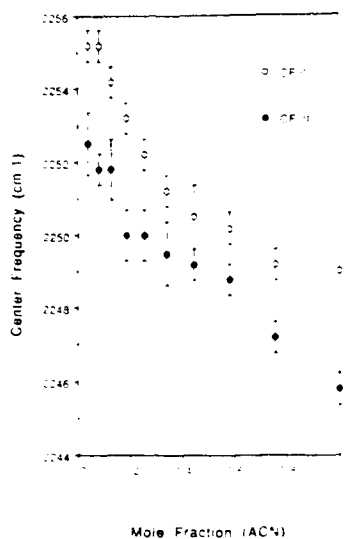


Figure 5 Center frequency as a function of concentration; error bars are  $\pm \sigma$

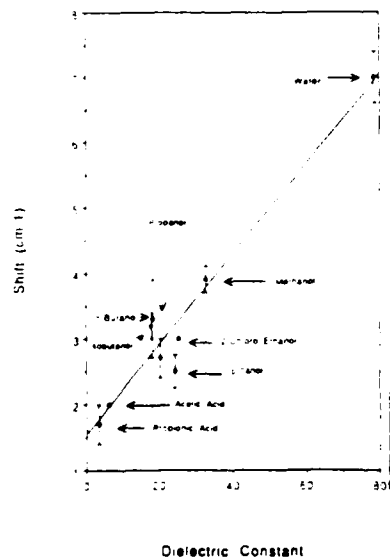
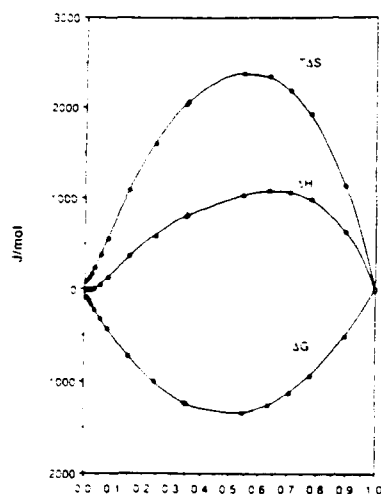


Figure 6 Shift, in  $\text{cm}^{-1}$ , from  $2249 \text{ cm}^{-1}$  for  $1.9 \text{ M CH}_3\text{CN}$  in a variety of protic solvents. The error bars are  $\pm \sigma$  from a minimum of three replicate measurements. The linear equation is  $y = 1.5 + 0.069x$ ,  $R = 0.97$ . All dielectric constant values were taken from ref. 39



Mole Fraction ACN

CAP00 : Figure 7 Excess thermodynamic properties of the CH<sub>3</sub>CN/water  
CAP06 : mixture.  $\Delta H^E$  from ref 43 and  $\Delta G^E$  from ref 31.

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